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ABAM

C5

Evaluation of Phase Partitioning Kinetics
at Waste Land Treatment Sites
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ABSTRACT

This research is examining phase partitioning kinetics of organic compounds among soil water, soil gas, oily sludge and soil solids phases. These compounds are introduced into soil systems by the application of oily sludges at land treatment sites of petroleum refineries. C-14 tracer techniques are being used to evaluate phenol, toluene, and 2-methyl naphthalene interphase transfer using both batch and column techniques. Flow-interruption techniques have merit for soil columns compared to continuous injection. This paper is limited to defining techniques and giving representative results, as work is ongoing. The results of this work are being used to assess the local equilibrium assumption of conventional assessment models.

1. **Introduction**

Our present understanding of the persistence and migration of toxic organics in industrial waste land treatment systems is limited by several deficiencies. One major deficiency is our understanding of the rate of release of toxic organics from the relatively immobile soil and waste phases to the highly mobile water and air phases of the unsaturated zone.

In land treatment systems, many nonsteady-state processes occur. Intermittent application of waste, periodic rainfall, adsorption, desorption, volatilization, and the release of toxic contaminants from the applied waste are examples of nonsteady-state processes. In the past, the behaviour of operating sites has been analysed using mathematical models which employ steady-state or time-invariant approximations for many of these processes (e.g., EPA's RITZ land treatment model). Nonsteady-state processes may be important for evaluating decommissioning and clean-up of abandoned sites. The validity of these approximations is the subject of this research.

The broad objective of this study is to define and evaluate nonsteady-state effects in industrial waste land treatment systems with particular reference to the mobility of toxic organics in decommissioned sites. The research includes:

1) a determination of the kinetics of adsorption, desorption, volatilization, and waste solvent - water partitioning for three toxic organics applied in the form of oily wastes to two operating land treatment sites; and

2) a formulation of a mathematical model of four-phase (soil, water, air, waste) partitioning which includes kinetic effects, and its comparison to the local equilibrium assumption. Future work will need to include an evaluation of soil column results under conditions of intermittent infiltration and nonsteady-state waste application.

The work reported in this paper is ongoing at the time of writing. Accordingly, this paper is limited to defining the techniques being used and to giving related results.

2. Literature Review and Conceptual Model

Previous research into the fate of toxic organics in soil systems has primarily focused on pesticides (references 1-4). Much of this research has attempted to include sorption kinetics and other non-equilibrium effects (2). Some studies have included the air phase and the possibility of volatilization (3). Very recent research has examined the effect of discontinuous infiltration and found that greater leaching was observed under steady-state flow conditions than under non-steady conditions. The authors hypothesized that the herbicides tested were allowed to migrate to more stable adsorption sites during the no-flow intervals (4). These recent findings support earlier theories that soil-water partitioning may be a two-stage process which cannot be properly modelled without considering kinetic effects (2).

The behaviour of industrial and municipal contaminants in groundwater has been an active field of research by hydrogeologists (5). Some of this research has demonstrated kinetic effects (6). Unfortunately, the absence of an air phase and the resulting physico-chemical differences mean that many of the phase-partitioning findings from groundwater studies need to be re-examined to determine their applicability to surface soil problems.

Phase partitioning is also an important topic in other fields of environmental research. The correlation of partitioning parameters with other chemical properties has been examined (7). The sensitivity of water quality models to partitioning parameters has prompted interest in models which include kinetic effects and two-stage adsorption in bed sediments (8). A refreshingly different approach to phase partitioning has been the fugacity methods currently receiving much attention (9).

Research into the land treatment of toxic wastes is complicated by the presence of a fourth phase, the solvent in which the wastes are applied to the site. Recent work has focused on the treatability of wastes under different soil and operating conditions and the development of comprehensive models (10-12). These models deal only with time-averaged, steady-state behaviour of operating sites and they presently rely on assumptions of instantaneous phase partitioning equilibrium.

A conceptual model of the four phases is given in Figure 1. The contaminant of concern is initially applied to the land system in a relatively immobile, oily sludge form. Subsequent redistribution transfers the contaminant into water, air and soil phases. The contaminant is transported out of the plow zone by gaseous diffusional processes and by infiltrating rain water. Due to intimate contact between soil water and all other phases, land treatment systems commonly consider interchange between the following phases:

- i) waste - water (K_w);
- ii) air - water (K_a); and
- iii) soil - water (K_d).

The coefficients indicated in Figure 1 are the equilibrium description of interphase relationships. Waste-air and soil-air interchange appear to be negligible except in extremely dry conditions. Movement of contaminants in aqueous phases is assumed to occur only with advection dispersion processes associated with water transport due to the relative immobility of the waste.

3. Batch Methods for Determining Phase Partitioning Coefficients

A set of batch procedures for determining equilibrium and kinetic phase partitioning coefficients were developed and tested. The methods use carbon-14 tracers to allow accurate and inexpensive measurement of concentrations. A typical procedure involves adding carbon-14 labelled compound to a reactor containing two of the phases. The reactor is tumbled to allow equilibration and then centrifuged to separate the phases. Both phases are then analysed to determine the concentration in each over time.

Phase partitioning data obtained from batch tests violates some of the underlying assumptions of ordinary linear and non-linear least squares. Previous work has demonstrated that the application of ordinary regression methods to such data can produce very poor estimates of equilibrium parameters. A method known as error-in-variables method or EVM was used to analyse our data. The results are shown as black lines in Figure 2 (13) for toluene in sludge and soil from a refinery waste land treatment facility near Nanticoke, Ontario. They are maximum likelihood estimates of the equilibrium phase partitioning coefficients. The EVM approach can also be used for non-linear isotherm models. It reduces to simpler regressions when they are appropriate. Criteria for choosing the best regression method can be obtained by starting with an EVM formulation.

Kinetic effects were evaluated in a batch system for all of the interphase transfers indicated in Figure 1. Primary emphasis was placed upon: air-water, soil-water, and sludge-water. Results from the equilibrium measurements were used to estimate rate coefficients and then a mathematical model of interphase kinetics for batch systems used to establish the most appropriate experimental conditions (e.g., solid:solution ratio). A rigorous quality control program allowed evaluation of the various uncertainties of the measurements.

The results of these batch, laboratory scale experiments, indicated that air-water transfer is at equilibrium for three compounds (phenol, toluene, 2-methyl naphathlene) within 1-2 hours. Scale-up to field scale considering the large difference in surface area suggests that equilibrium is attained within a few minutes. Evaluation of sludge-water kinetics was made by injecting the three C-14 labelled compounds into the sludge phase. The kinetics (Figure 3) were relatively noisy due to the small amounts of sludge (0.1 to 10 g) typically used. The small amounts are required experimentally due to their relatively large partitioning into the oil/sludge phase. The data suggests that equilibrium was obtained within an hour for the 3 organic compounds tested in these mixtures.

4. Column Methods for Determining Phase Partitioning Coefficients

Column breakthrough curves allow better estimates of water-solid partitioning kinetics than do batch techniques. A tritium pulse is first used to evaluate residence time/dispersion mechanisms and then C-14 tracer applied to evaluate partitioning kinetics. Both continuous injection and flow-interruption techniques (Figure 4) have been used experimentally.

These conventional techniques can be used for weakly sorbing substances. But strongly sorbing substances (eg., 2-methyl naphthalene) have extremely long residence times of the order of a month or more, especially in high organic matter clay soil. A co-solvent approach (14, 15) was used to increase migration times by increasing the tendency for the chemical to partition into the fluid phase. Results, given in Figure 5, demonstrate that co-solvent data can be extrapolated to aqueous systems.

5. Application of Results

The application of these results of this study is directed, at present, to evaluating the limitation of models which assume equilbrium partitioning.

A very practical problem which can limit the applicability of these models is the spatial variability of soil systems and hence of the phase partitioning coefficients. Soil and waste samples from ten locations at the Nanticoke treatment site have been analysed to deetermine the spatial variability of model parameters. Preliminary calculations show that the effect of phase partitioning can affect predicted infiltration by 100%.

The local equilibrium assumption (LEA) can be assessed by examining combinations of transport velocity and the rate at which partitioning equilibrium is attained. One form of the results is given in Figure 6. It shows the region of LEA applicability for modelling steady-state saturated flow. For example, this chart can be used to relate sorption kinetics onto soil to rates of water movement. Simultaneous inter-relationships of all four phases can be evaluated using a transport model.

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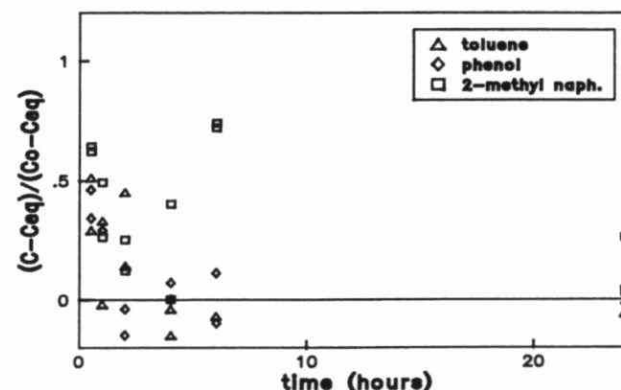15. Fu, J.K. and R.G. Luthy (1986). J. Environ. Engr., ASCE, 112(2), pp. 328-345.

figure 3. Results of sludge—water batch kinetics study. Y—axis shows initial concentration (C=Co) at y=1, equilibrium (C=Ceq) at y=0.
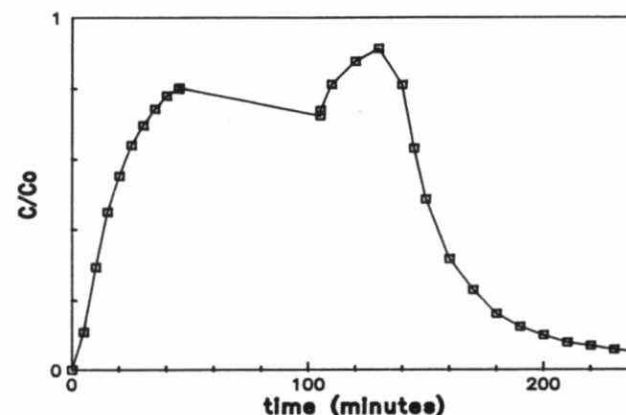

figure 4. Example of flow—interruption btc. Flow stopped from 45 minutes to 105 minutes. Decrease in effluent concentration after interruption is evidence of non—equilibrium effect.
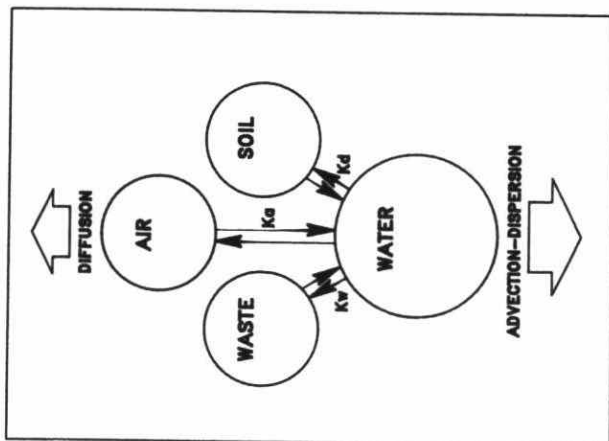
figure 2. Phase partitioning isotherms for toluene (batch results).

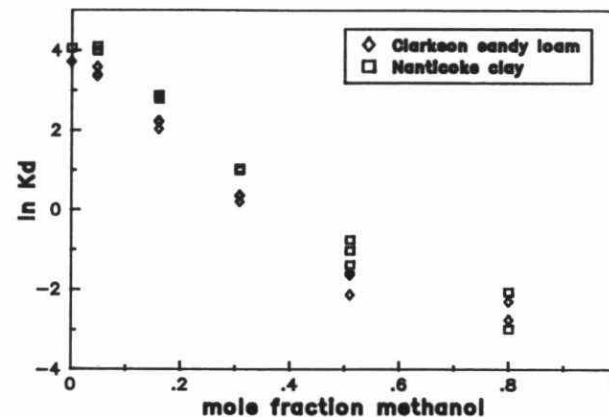figure 1. Phase partitioning and transport in land treatment systems.

figure 5. Effect of cosolvent on soil-water equilibrium coefficients. Note that log-linear relationship allows extrapolation to aqueous conditions.
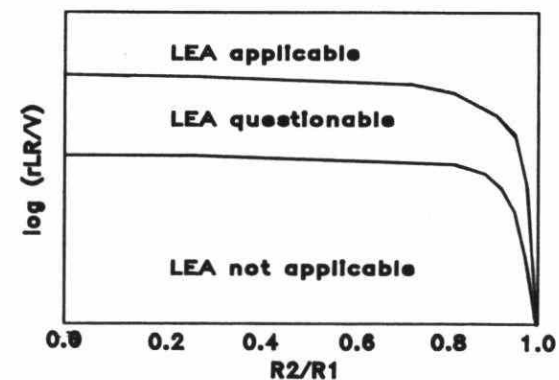

figure 6. Region of LEA applicability for modelling sorption in steady, saturated flow. Y-axis shows ratio of reaction rate (r) to transport time scale (V/RL). X-axis shows ratio of retardation factors with (R1) and without (R2) the kinetically controlled phase.